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Manganese in Narragansett Bay

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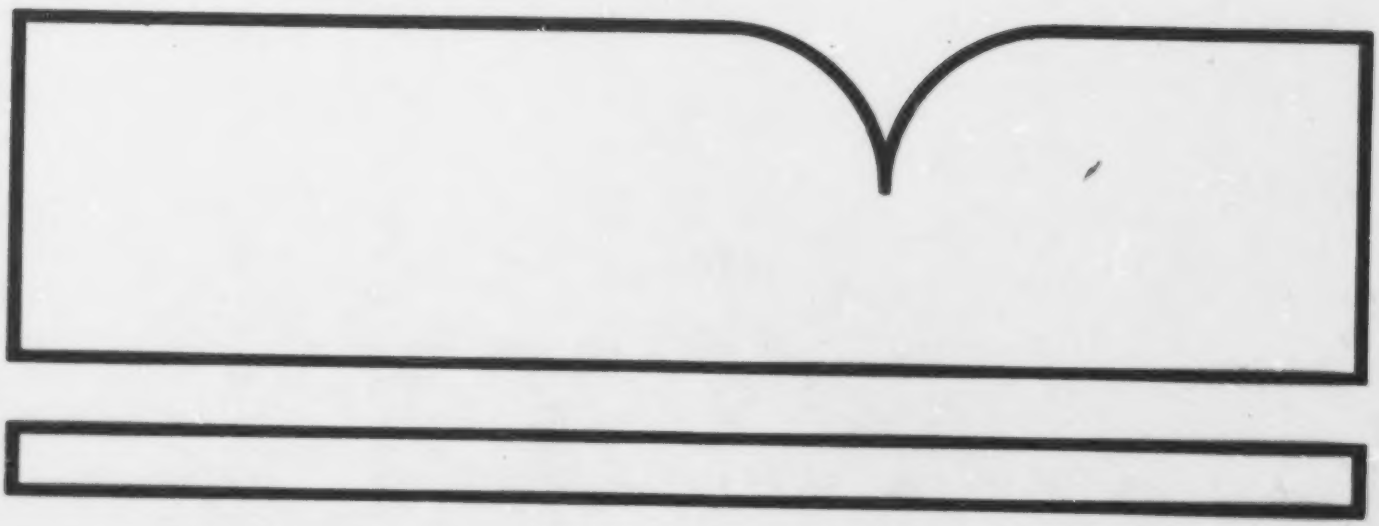

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By William F. Graham, Michael L. Bender, and Gary P. Klinkhammer

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16. ABSTRACT

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The flux of dissolved manganese into bottom waters was about 2± 1μg cm^{-2} d^{-1}. Concentrations in bottom waters are high relative to surface waters.

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Manganese in Narragansett Bay[1]

William F. Graham, Michael L. Bender, and Gary P. Klinkhammer
Graduate School of Oceanography, University of Rhode Island, Kingston 02881

Abstract

Concentrations of dissolved manganese and particulate manganese and aluminum were determined in samples from Narragansett Bay, Rhode Island, and its surrounding rivers. Total manganese is approximately conservative, but dissolved and particulate manganese are not. Desorption may occur in the tidal rivers at low salinities. Most riverine manganese is dissolved but manganese in the bay is predominantly particulate, probably due to rapid manganese oxidation at bay water pH.

The flux of dissolved manganese into bottom waters was about 2 ± 1 μg cm^{-2} d^{-1}. Concentrations in bottom waters are high relative to surface waters.

Changes in ionic strength and pH resulting from the mixing of fresh and salt water in estuaries may produce significant changes in the phase distribution of metals. Soluble metals may be adsorbed, flocculated, or precipitated, while those present in a particulate form may be dissolved or desorbed (Kharkar et al. 1968; Murray and Murray 1973; Boyle et al. 1974). For several reasons, manganese is of special interest. Under various environmental conditions, manganese can be either highly mobile (Lynn and Bonatti 1965; Li et al. 1969) or highly reactive and insoluble (Stumm and Morgan 1970); its behavior in estuaries may therefore be more dramatic than that of other transition metals. The very high concentration of dissolved manganese in pore waters of nearshore sediments has been well documented, and diffusion of manganese into bottom water may be important in the estuarine balance of that element. A knowledge of manganese behavior in estuaries is relevant to understanding the causes of high concentration in pelagic sediments. Manganese is one of the most abundant reactive metals in river water (Turekian 1971), and precipitation of manganese oxyhydroxides in estuaries may provide a phase to host removal of other elements.

Mixing of fresh and salt waters can apparently cause both dissolution and precipitation of manganese. Evans and Cutshall (1973) found that manganese associated with particulate matter in the Columbia River was released when mixed with seawater. Conversely, Lowman et al. (1966) found that soluble manganese in Puerto Rican river water was precipitated when mixed with seawater. Windom et al. (1971) also found that manganese from three rivers in the southeastern United States was precipitated when salt water was encountered.

We have determined the content of dissolved and particulate manganese in water samples from Narragansett Bay (Rhode Island) and its surrounding rivers and have also measured fluxes of dissolved manganese across the sediment–water interface. The results of our study indicate, we believe, that adsorption-desorption phenomena, oxidation of soluble manganese to insoluble compounds, and diffusion out of sediments occur in the estuary and are major features of the manganese cycle.

We are grateful to C. Oviatt and S. Nixon for accommodating us on sampling cruises in Narragansett Bay, and to them and N. Luedtke for providing manganese samples from benthic flux experiments. J. Simpson, J. Edmond, and E. Boyle did much to stimulate our interest in estuarine geochemistry. Neutron irradiations and gamma counting were carried out using the facilities of the Rhode Island Nuclear Science Center.

[1] Financial support for this work was provided by grant R 803243-01-0 from the Environmental Protection Agency.

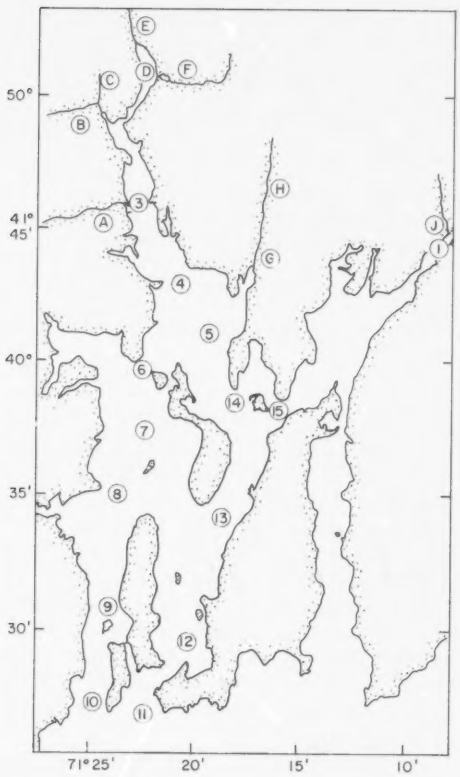

Fig. 1. Sampling stations taken in Narragansett Bay and surrounding rivers.

Materials and methods

Collection of water samples—Water samples were collected in July 1973 at eighteen stations in Narragansett Bay and at seven stations in the rivers which supply freshwater to it (Fig. 1). Bay samples were taken 1 m below surface and 1 m above bottom. Because the rivers were very shallow at this time of year, only one mid-depth sample was taken at each river station. Four samples of coastal water were collected in October 1973, near Block Island in Rhode Island Sound, 11 km from the mouth of the bay, at 2-, 8-, 14-, and 20-m depth.

The bay samples were collected with 2-liter Niskin bottles from the URI research cruiser *Crow's Nest*. River samples were taken from a conveniently located bridge with a glass sampling bottle. The Block Island samples were collected by the RV *Trident* on cruise 145 with 5-liter Niskin bottles. All samples were stored frozen in acid-washed linear polyethylene bottles at –5°C until analysis. There does not seem to be any significant difference between samples that were frozen and those that were filtered immediately (Table 1).

Table 1. Comparison of the amount of manganese found in frozen and unfrozen samples.

Sample No.	Dissolved Mn µg/kg Frozen	Unfrozen	Particulate Mn µg/kg Frozen	Unfrozen
1	118	112	5.4	4.5
2	114	121	4.4	4.5
3	169	161	—	—
4	163	155	—	—
5	155	149	—	—

Analytical methods for water samples—For analysis, samples were thawed and about 500 ml filtered through an acid-cleaned 47-mm Millipore filter (0.45 μ). The filtrate was acidified with 1 ml of concentrated HCl, and the filters were dried at 80°C and stored in acid-cleaned vials until irradiation.

The filtrate was analyzed for dissolved manganese by a radioisotope dilution neutron activation technique modified from that of Slowey and Hood (1971). ^{54}Mn was added to each sample and the solution was allowed to equilibrate for 36–48 h. The pH was then adjusted to 8 with 1 N and 0.1 N NH_4OH. The sample was extracted twice with 8 ml of 0.1 M 8-hydroxyquinoline in chloroform. Extraction efficiencies, as measured by a count of ^{54}Mn spike, ranged from 85–97%, average value 94%. The chloroform extracts were combined and back-extracted into 1 ml of 0.2 N HNO_3. Back extraction efficiencies were between 45 and 74%, average 57%. Overall extraction efficiency for the process averaged 54%.

The acid extract was transferred to acid-cleaned vials, evaporated to dryness at

80°C, and sealed for irradiation. The sealed samples were irradiated for 2 min in the Rhode Island Nuclear Science Center swimming pool reactor at a flux of 4×10^{12} n cm^{-2} s^{-1}. About 1 h after irradiation the samples were transferred to an unirradiated vial with 0.75 ml of concentrated HNO_3 and counted for 400 s on a Ge(Li) detector (resolution of 2.3 keV for the 1,332 keV gamma ray of ^{60}Co) coupled to a Nuclear Data 2200 4096 channel analyzer with a computer-compatible magnetic tape output (Ampex TM-7) for spectrum analysis. A computer program (J. L. Fasching personal communication) was used to process the Ge(Li) spectra acquired. The samples were analyzed for ^{54}Mn at 835 keV and ^{56}Mn at 847 keV. Standards consisting of $Mn(NO_3)_2$ equivalent to 1 μg of $^{55}Mn^{2+}$ in 1 ml of ^{54}Mn tracer of the same activity as added to the unknown samples were irradiated and counted in the same manner as the unknown samples. After correction of all ^{56}Mn count rates back to the time of end of irradiation, the amount of ^{55}Mn in the unknown was calculated from the formula:

$$^{55}\text{Mn (unknown)} = \frac{(C\ ^{56}\text{Mn}/C\ ^{54}\text{Mn})\ \text{unknown} \times \mu\text{g}\ ^{55}\text{Mn (std)}}{(C\ ^{56}\text{Mn}/C\ ^{54}\text{Mn})\ \text{std}},$$

where C is the count rate.

Precision of the method, determined on a suite of nine samples run in duplicate, is ±5% (1σ). Blanks on the river and bay samples, determined by re-extracting previously extracted samples, were 0.3 ppb. Blanks on Block Island Sound samples averaged 0.06 ppb. All results were corrected for the blanks found.

Concentrations of particulate Mn and Al were also determined by neutron activation. The vials containing the filters were irradiated for 5 min in the reactor and counted exactly 7 min after irradiation began. Absolute standards for aluminum and manganese were prepared by evaporation of suitable amounts of Al and Mn atomic absorption standards into vials identical with the sample vials. These standards were then irradiated and counted in the same manner as the unknowns. Constant geometry was maintained during the counting of all standards and unknowns. Corrections were made for dead time and half-life discrimination. Precision of the method, determined on a six-sample replicate, was ±5% for Mn and ±4% for Al. Blanks were equivalent to 0.12 μg kg^{-1} for Al and 0.04 μg kg^{-1} for Mn. These levels amounted to 0.04% of the aluminum and 4% of the manganese in the samples.

Techniques for measurement of the benthic flux of manganese—Benthic fluxes of manganese were determined by the procedures of Hale (1974). Two PVC chambers with open bottoms (area about 2,500 cm^2, average height 11 cm) were placed on the sediment. Six samples were taken during each experiment: one of bottom water when the chambers were emplaced, one 3 h later from a dark bottle filled at the start of the experiment with bottom water, one from each of the two chambers at the start of the experiment, and one from each of the chambers 3 h later. The solutions were filtered through 0.45-μ Nuclepore filters aboard ship immediately after collection, acidified to pH 2, and subsequently analyzed by atomic absorption spectrophotometry using direct injection into a Perkin-Elmer HGA-2100 graphite furnace. The experiment was carried out nine times during June and July 1975; results are summarized in Table 2. Benthic fluxes for each chamber are calculated from the formula

$$\text{Flux} = \frac{(\text{final concn} - \text{initial concn}) \times (\text{chamber vol})}{(\text{chamber area}) \times (\text{length of experiment})}.$$

Since manganese concentrations in bottom water and dark bottle samples were generally the same (except on 24 June when the dark bottle sample was apparently grossly contaminated), they were apparently not altered by the 3-h incubation. The similarity also implies that our collection procedures did not randomly

Table 2. Results of experiments to determine benthic flux of manganese. Final samples were taken 3 h after start of experiment.

Experiment date	Manganese concentration, ppb						Flux, μg cm^{-2} d^{-1}	
	Initial bottom water	Final dark bottle water	Chamber II samples		Chamber III samples		Chamber II	Chamber III
			Initial	Final	Initial	Final		
24 Jun	16	98	18	53	16	36	3	2
26 Jun	10	12	16	60	17	51	4	3
1 Jul	8	7	17	442	17	69	37	5
3 Jul	9	9	26	40	16	41	1.2	2
10 Jul	8	7	9	21	31	261	1.1	20
15 Jul	12	12	14	42	12	46	2	3
22 Jul	18	18	21	46	22	46	2	2
29 Jul	15	16	16	50	16	45	3	3
31 Jul	21	29	31	38	29	52	6	1.1

contaminate the samples and that the analytical precision was good.

The first five times the experiment was done the manganese in the initial chamber samples was generally higher than in the bottom water samples, probably due to pore waters introduced as the sediment inside the chambers was disturbed during emplacement. If pore waters at the sediment–water interface contain 1 ppm dissolved Mn, then about 1 mm of sediment would raise the manganese concentration in the initial chamber sample to a value 10 ppb above the ambient bottom water concentration. This does not seem unreasonable. During the course of the summer, our sampling techniques improved and samples collected on the last 4 days showed little evidence of having been stirred.

For the most part, results were consistent throughout each experiment. However, the final samples from chamber 2 on 1 July and chamber 3 on 10 July were apparently grossly contaminated, and fluxes calculated from these experiments are not considered in the discussion below.

Results and discussion

Narragansett Bay is a large, relatively homogeneous water body. Our samples were collected from the bay and the freshwater–salt water mixing zones of several tidal rivers (Tables 3 and 4, Fig. 1). When samples (other than benthic flux samples) were collected, salinities ranged from about 24‰ at the mouth of the Providence River to 32‰ in Block Island Sound at the mouth of the bay. Comparing the concentration of a tracer with salinity is useful in studying its behavior in an estuary (*see* e.g. Boyle et al. 1974). In the case of Narragansett Bay it is not appropriate to lump all samples together. The manganese distribution within each tidal river should be considered using the salinity and manganese concentration of bay water at the mouth of the river as one end member, and obviously each tidal river should be considered individually. For the open bay, we make the assumption that the river input is well mixed at the north end of the bay. Thus, the manganese may be investigated as a single-valued function of salinity within the salinity range found in the bay itself.

Total Mn values are plotted against salinity in Fig. 2, and a conservative mixing line has been drawn. Tie points are the weighted average freshwater total Mn content based on typical July river flow data

Table 3. Dissolved manganese and particulate manganese and aluminum in Narragansett Bay.

Sta.	Depth m	S ‰	Manganese Diss. µg/kg	Manganese Partic. µg/kg	Aluminum Partic. µg/kg
3	1	24.26	60	5.4	56
	12.5	29.02	22	15	465
4	1	24.20	26	27	60
	6	27.99	12	22	155
5	1	25.61	5.4	29	37
	6	31.00	6.9	14	125
6	1	25.04	3.3	31	101
	12.5	28.36	20	19	416
7	1	27.31	3.8	25	89
	6	27.72	15	16	160
8	1	25.81	5.0	24	62
	11	29.07	9.5	14	141
9	1	27.07	4.4	18	101
	11	29.81	3.1	13	111
10	1	28.55	2.3	11	67
	16	30.04	2.4	4.2	82
11	1	29.11	1.8	4.5	58
	16	30.32	1.9	2.6	43
12	1	25.45	3.1	20	65
	11	30.37	1.8	3	46
13	1	29.26	1.9	5.9	32
	11	29.18	1.7	6.8	56
14	1	25.26	3.6	27	34
	11	29.87	5.8	9.4	287
15	1	24.62	8.8	32	50
	13	29.66	6.0	15	228
Block Island	2	32.2	0.6	1.1	31
	8	32.2	0.5	1.1	34
	14	32.2	0.5	1.1	36
	20	32.2	0.8	1.0	35

(U.S. Geol. Surv. 1974) and the Mn content of the Block Island Sound samples: 190 μg kg^{-1} and 1.5–1.8 μg kg^{-1} respectively. The conservative mixing line drawn through the plotted points suggests that total manganese is neither gained nor lost during its passage through the open bay at this time of year. This also appears true

Table 4. Dissolved manganese and particulate manganese and aluminum in rivers feeding Narragansett Bay.

Sta.	Depth m	S ‰	Manganese Diss. µg/kg	Manganese Partic. µg/kg	Aluminum Partic. µg/kg
A	mid	<0.2	204	4.4	29
B	mid	<0.2	55	16	100
C	mid	<0.2	577	6.7	409
D	1	19.67	73	2.4	53
E	mid	<0.2	124	40	92
F	mid	<0.2	97	115	268
G	mid	10.94	99	4.7	88
H	mid	<0.2	60	10	49
I	mid	4.83	174	8.1	257
J	mid	<0.2	232	43	179

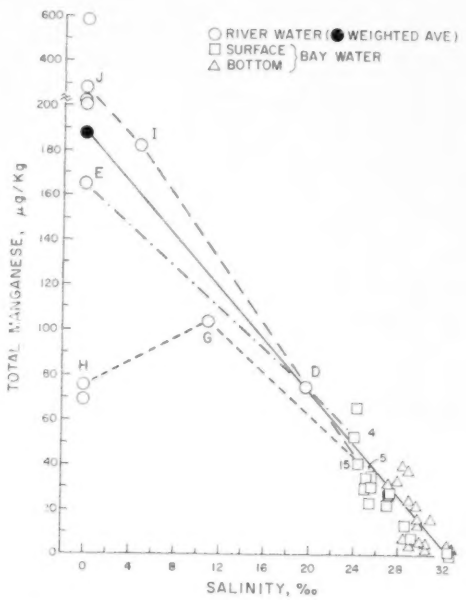

Fig. 2. Total manganese vs. salinity.

of two of the three tidal rivers: the total manganese concentration at station I can be roughly explained as a mixture of J and 15, at station D as a mixture of E and 3. Samples G and H are anomalous in this respect.

Although the behavior of total manganese in the bay may be nearly conservative, this is certainly not true for the dissolved and particulate fractions. Particulate manganese (Fig. 3) drops from the average river concentration of 28 μg kg^{-1} to about 5 μg kg^{-1} at the first saline water. We have only three samples in the low salinity (<20‰) range, but the change in the ratio of particulate manganese to particulate aluminum between the river and the low salinity bay samples also indicates release of manganese. The ratio of particulate manganese to particulate aluminum declines from an average value of 0.21 in the freshwater rivers to 0.03–0.05 in these narrow freshwater–salt water mixing zones.

At higher salinities, however, a reversal takes place. At about 24‰, which corresponds to the north end of the bay, the

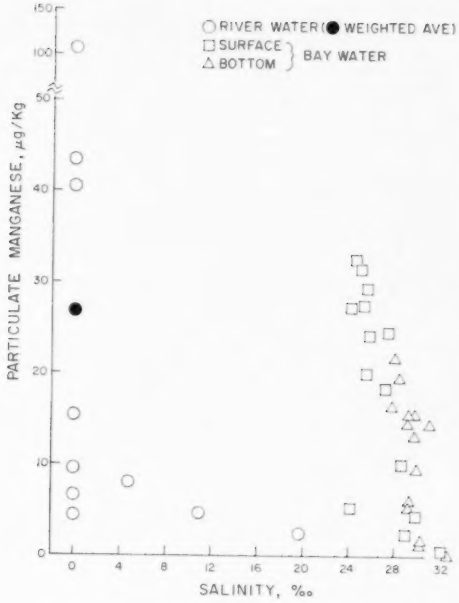

Fig. 3. Particulate manganese vs. salinity.

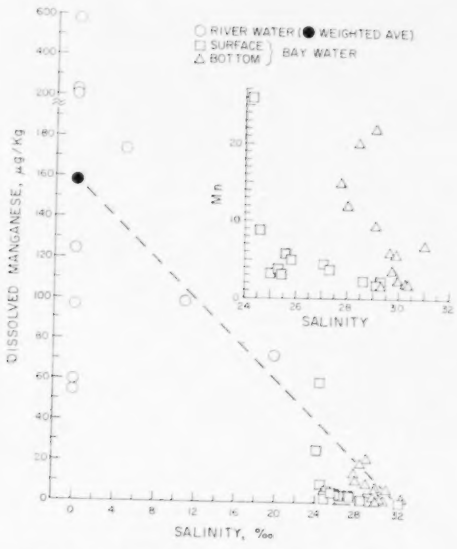

Fig. 4. Dissolved manganese vs. salinity.

particulate manganese increases sharply (Fig. 3). Above 24.5‰, particulate Mn concentrations decline steadily on a line which might be interpreted as conservative. The increase in the particulate Mn content of the bay water at about 24‰ is mirrored by a drop in the level of dissolved Mn of surface water at the same salinity (Fig. 4). The bottom water samples, on the other hand, show a smaller deviation from a conservative mixing line and, for a given salinity, have consistently more manganese than surface samples.

We can therefore draw four significant conclusions about manganese in Narragansett Bay: total Mn is approximately conservative; there may be desorption of particulate Mn at low salinities (although this conclusion should be considered tentative, since it is based on only three samples); most manganese in the bay is particulate, whereas most manganese in rivers is dissolved; and dissolved Mn comprises a much higher fraction of the total in bottom waters than in surface waters.

Manganese is apparently desorbed from particulate material at the freshwater–salt water interface in the tidal rivers of Narragansett Bay, as in the Columbia River (Evans and Cutshall 1973). Picer et al. (1973) found in a laboratory study that manganese was desorbed from limestone or sediment as the salinity was increased from zero to 18‰; above 18‰, the distribution coefficient remained constant. From laboratory study of Cu and Co adsorption onto clays, O'Connor (1974) calculated that, at river pH values of 6 or higher, manganese will be desorbed as salt water is encou[illegible]d. Whether mixing of river water having a pH between 6 and 8 with seawater favors adsorption or desorption is determined by the dominant of two opposing processes. As river water is mixed with seawater the pH rises, and this favors metal adsorption since there are fewer protons around to compete with metals for adsorption sites. But as river water mixes with salt water, ionic strength and, hence, ion pairing increases, with an attendant decrease in the metal ion activity on which adsorption depends. In addition, competition for sites from divalent cations in seawater further depresses manganese

Table 5. Range of pH and percentage of dissolved manganese in Narragansett Bay surface and bottom waters and in surrounding rivers.

Location	pH range	Percent dissolved Mn	
		Range	Average
Rivers	4.2-7.0	46-99	85
Bay			
Bottom	7.6-8.0	19-51	32
Surface	7.9-8.3	10-29	15

adsorption. The rivers in our study (with one exception) ranged from pH 6.6 to 7.1. (The Mashassauk had a pH of 4.15, but contributes only 3% of the freshwater flow to the bay.) The Columbia River has a pH range of 7.7–8.5 (U.S. Geol. Surv. 1972). Laboratory and field studies appear to be in agreement, then, in indicating manganese desorption at low salinities.

Windom and coworkers (personal communication) have found that, in organically rich rivers typical of the southeast United States, organic-metal complexes are formed which flocculate on entering saline water. If this process does occur in Narragansett Bay, it is evidently overshadowed by the competing desorption processes.

A further question is why, although most of the manganese entering the bay is dissolved, most of the manganese in the bay is particulate. Hydrogen ion concentration may be important in determining the distribution of manganese between different phases. Unfortunately, data for our bay water samples are not reliable. However, there are some pH data for five bay stations temporally and geographically similar to ours (Chowder and Marching Soc. 1967). A summary of the available pH data, compared with the fraction of manganese in the dissolved phase, is given in Table 5.

In Fig. 5, we have plotted our data along with those of Windom et al. (1971) from three rivers in the southeast United States. From all these data we conclude that physical and chemical processes that are strongly pH dependent must play a major role in determining manganese distributions in

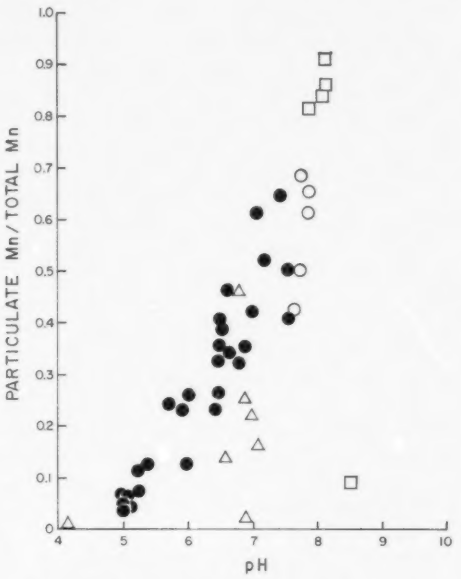

Fig. 5. Fraction of manganese in the particulate form vs. pH. This study: △—river samples; ○—bay bottom water; □—bay surface water. Windom et al. (1971): ●.

natural waters. The pH-related processes most likely to be at work here are those of adsorption and oxidation, and two strong arguments point to oxidation as the key process. First, the physicochemical arguments of O'Connor (1974) indicate that manganese is more likely to be dissolved in bay than in river water. Second, in the waters of Narragansett Bay, the particulate Mn accounts for between 3 and 9% of the estimated inorganic suspended matter (assuming that the aluminum concentration of the suspended matter is 8%). That this amount of manganese can be truly adsorbed onto the suspended matter of the bay seems unlikely.

The oxidation of dissolved Mn(II) to highly insoluble Mn(IV) compounds such as MnO_2 has been investigated in great detail by Hem (1963*a*,*b*,*c*) and Morgan (1967). Variables controlling the rate of oxidation were found to be pH, oxygen partial pressure, and the presence of catalysts. When the oxidation rate is catalyzed

by particulate matter such as feldspathic sand, the reaction becomes first order (Hem 1963*b*,*c*). From Hem (1963*c*) we can estimate a first order rate constant for a pH of 8.2 and a zero partial pressure of 0.2 atm of 3.3×10^{-4} min^{-1}. This corresponds to a half-life of about 2 days. Morgan and Stumm (1964) have shown rapid flocculation of manganese dioxide in the presence of manganous ion. As the residence time of the water in Narragansett Bay during summer is on the order of a month, it is not surprising that most manganese in the bay is in the particulate form.

Precipitation of manganese as manganese carbonate is an alternative explanation which appears unlikely to us. On the basis of the phase diagrams of Morgan (1967), the waters of the bay are undersaturated with respect to manganese carbonate by a factor of 3 to 20.

Finally, we consider the question of why dissolved Mn concentrations in deep waters are higher than in surface waters. Two possible causes are the low pH of bottom waters relative to surface waters (due to the presence of CO_2 from oxidation of organic matter) and the migration of dissolved Mn out of pore waters. The first is unlikely, since the pH difference between deep and surface waters is only a few hundredths of a pH unit. To evaluate the second possibility, we did the benthic flux experiments in which we measured the rate of manganese migration out of sediments. Calculated values of fluxes are given in Table 2. Most of the values fall in the range of 2 ± 1 μg cm^{-2} d^{-1}. (There is considerable variability, ascribed to patchiness in the benthic community and sediment lithology, temporal changes in sediment geochemistry due to high biological activity during summer months, temperature effects, and surely experimental artifacts.) A typical value for the total manganese concentration in the bay is about 30 μg kg^{-1}, and the average depth of the bay is about 10 m; thus the average "standing crop" of manganese at the time of our sampling was about 30 μg cm^{-2}. With a benthic flux of 2 μg cm^{-2} d^{-1} we calculate a "doubling time" for total manganese of 15 days. Thus if our values of manganese benthic fluxes are at all representative, there is no problem in accounting for the increase in dissolved Mn in the bottom water by migration out of sediments. We believe this to be the dominant process leading to the higher proportion of dissolved Mn in bottom than in surface waters.

Conclusions

The throughput of manganese in the Narragansett Bay estuary appears to be largely conservative, with no evidence of a major net input or removal through interaction with the sediments of the bay, at least during summer; different results might be obtained at other times of year.

Particulate Mn is apparently desorbed at the freshwater–salt water interfaces of the bay. Within the bay, manganese is converted from the dissolved to the particulate form. The driving force behind this conversion appears to be a pH shift; the mechanism, while not well understood, is very likely oxidation of dissolved Mn to particulate manganese dioxide, coupled with interactions between the adsorption and oxidation processes.

Diffusion of dissolved Mn out of sediments is fast enough to be a major factor in the manganese budget of the bay and is probably the cause of the enrichment of dissolved Mn in deep over surface waters.

The high benthic flux emphasizes the fact that bay waters form an open system with respect to exchange of manganese with sediments. Dissolved manganese may be gained through migration out of sediments; particulate manganese may be removed by inorganic and biogenic sedimentation. Why then is total manganese approximately conservative? There are three possible interpretations. First, our measured benthic fluxes may be atypically high, and the gross fluxes of manganese across the sediment–water interface small relative to the river input of manganese to the bay. Second, fluxes across the interface may be large but were fortuitously in balance when the samples were taken. Finally, fluxes may be large but the net

flux may be zero due to continous remobilization of dissolved Mn from bay sediments.

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